Viscosity in an Electric Field of Mixtures of Polar Gases with Argon and Helium

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The influence of an electric field on the viscosity of mixtures of polar gases with argon and helium has been measured using a capillary bridge. The relative change of the viscosity coefficient \( \eta \) has been obtained in this way. A theory of the effect is sketched along similar lines to those followed by Tip for the magnetic case. The half value of the field is shown experimentally to be linear in the concentration. Moreover, a comparison of the experimental data with the theory yields cross section ratios of noble-polar collisions versus polar-polar collisions, both for the reorientation and for rotational energy transfer. The reorientation collision frequencies are compared to those obtained from non-resonant microwave absorption.

Introduction

The study of the Senftleben effect, i.e., the transport properties of polyatomic gases in external fields is a useful tool for the investigation of the non-spherical part of the intermolecular interaction and the mechanism, not yet fully understood, for internal energy transfer in such gases.

As has been shown in a previous paper, hereafter referred to as I, the change in the viscosity of a polar gas in an electric field occurs at higher and higher molecular precession frequencies as the dipole moment of the molecule increases.

This shows, in agreement with the existing theories, that the half-saturation field value of the dispersion-like saturating curve, typical of this class of phenomena, is proportional to a cross section for molecular reorientation that increases with the molecular dipole moment.

However, a more direct test of the theory is afforded by mixtures, whose concentration is an additional parameter, easy to vary experimentally and unequivocal in nature.

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8 A. TIP, Physica 37, 411 [1967].
11 N. TAXMAN, Phys. Rev. 110, 1235 [1958].
instead of the quantum-mechanical Waldmann-Snider equation\textsuperscript{13, 14}; besides Tip's theory concerns primarily viscosity in a magnetic, rather than electric, field.

In § I Tip's theory is recalled in a slightly modified and generalized form, apt to a treatment of the electric case. In § II the experimental apparatus and results are given. In § III the experimental data are compared to theory, whose results appear to be well verified, and the cross section ratios are obtained.

I. Theory

In this Section a theory of the field effect is sketched, using the same methods and notation employed for the pure gas in I. The present theory is essentially the same of Tip's, the main difference being that the field (super) operator will have the properties corresponding to the electric field.

From the start the treatment will be limited to binary mixtures of a polar gas $p$ with a noble gas $n$, corresponding to the experimental situation. In place of Eqs. (2) to (8) of I there will be then two Chapman-Enskog equations:

$$-2[W_p]^{(2)} = x_p \hat{g}_{pp} B_p + x_n \hat{g}_{pn} (B_p + B_n) - (i/\hbar) [H_{\text{field}}, B_p],$$

$$-2[W_n]^{(2)} = x_p \hat{g}_{np} (B_p + B_n) + x_n \hat{g}_{nn} B_n$$

where $x_p$ and $x_n = 1 - x_p$ are the concentrations. The viscosity is:

$$\eta = n k T (x_p \langle [W_p]^{(2)} : B_p \rangle + x_n \langle [W_n]^{(2)} : B_n \rangle).$$

It is convenient to introduce the field operator $\mathcal{F}$, defined by

$$\mathcal{F} X = - (i/\hbar) [H_{\text{field}}, X]$$

and the concentration-dependent collision operators

$$C_{pp} = x_p \hat{g}_{pp} + x_n \hat{g}_{pn},$$

$$C_{pn} = x_n \hat{g}_{pn},$$

$$C_{np} = x_p \hat{g}_{np},$$

$$C_{nn} = x_p \hat{g}_{nn} + x_n \hat{g}_{nn}.$$  

Moreover, the simple notations

$$K = \sqrt{2} [W_p]^{(2)}, \quad H = \sqrt{2} [W_n]^{(2)},$$

$$X = - \sqrt{2} B_p, \quad Y = - \sqrt{2} B_n$$

will be used. The tensorial character of the quantities involved will not be taken into account for the time being. Finally a scalar product will be defined as $n$ times the average of the product of two quantities: if the latter are tensors, the appropriate contractions shall be taken. With this simplified notation, Eqs. (1) become

$$K = C_{pp} X + C_{pn} Y + \mathcal{F} X$$

$$H = C_{np} X + C_{nn} Y$$

and Eq. (2) becomes

$$-\eta/k T = x_p (K, X) + x_n (H, Y).$$

Equations (7) and (6) should be compared to Eqs. (A1) and (A2) of I for the pure gas. From here on the treatment parallels closely the variational method for the pure gas used in Appendix A of I.

$X$ and $K$ are vectors of a Hilbert space $\mathcal{H}_p$, for which a basis $\{\psi_i\}$ will be chosen and the following properties assumed:

$$\psi_i \equiv K; \quad C_{pp,ik} = 0 \text{ unless } i, k = 1, 2, \text{ or } k = i;$$

$$\mathcal{F} \psi_i = 0; \quad \mathcal{F}_{xx} = 0; \quad \mathcal{F}^\dagger = -\mathcal{F}.$$  

Analogously, $Y$ and $H$ are vectors of another Hilbert space $\mathcal{H}_n$. They will be taken to be parallel to each other with the definitions

$$\psi_0 \equiv H; \quad (H, Y) = Y_0; \quad C_{nn,00} = (H, C_{nn} H).$$

Finally, the operators $C_{pn}$ and $C_{np}$, mapping $\mathcal{H}_n$ into $\mathcal{H}_p$ and viceversa respectively, will be assumed to have the properties

$$C_{pn,0i} = C_{np,0i} = 0 \text{ unless } i = 1, 2.$$  

Moreover, the "diagonal" matrix elements of the collision (super)operators (and also $C_{pn,10}$ and $C_{np,01}$) will be considered to be large in comparison to the "non-diagonal" ones coupling $\psi_2$ to $\psi_1$ and $\psi_0$.

A variational procedure will be used by choosing in $\mathcal{H}_p$ the set $\{\psi_1, \psi_2, \psi_i\}$ (where $\psi_i$ is any vector such that $\mathcal{F}_{xi} = -\mathcal{F}_{xi} = 0$) and in $\mathcal{H}_n$ the only vector $\psi_0$. Then scalar products are taken of the Eqs. (6) with the vectors chosen, obtaining

$$1 = C_{pp,1i} X_1 + C_{pp,1i} X_2 + C_{pn,10} Y_0,$$

$$0 = C_{pp,2i} X_1 + C_{pp,2i} X_2 + C_{pn,20} Y_0 + \sum_k \mathcal{F}_{ik} X_k,$$

$$0 = C_{pp,ii} X_i + \sum_k \mathcal{F}_{ik} X_k, \quad (i = 3, 4, \ldots),$$

$$1 = C_{np,01} X_1 + C_{np,02} X_2 + C_{nn,00} Y_0.$$  

\textsuperscript{13} L. WALDMANN, Z. Naturforsch. 12a, 660 [1957].

\textsuperscript{14} R. F. SNIDER, J. Chem. Phys. 32, 1051 [1960].
In the field-free case, the Eqs. (11) become
\[ \begin{align*}
1 &= C_{pp,11} X_1^0 + C_{pp,12} X_2^0 + C_{pn,10} Y_0^0, \\
0 &= C_{pp,12} X_1^0 + C_{pp,22} X_2^0 + C_{pn,20} Y_0^0, \\
0 &= C_{pp,ii} X_i^0 \quad (i = 3, 4, \ldots), \\
1 &= C_{np,01} X_1^0 + C_{np,02} X_2^0 + C_{nn,00} Y_0^0.
\end{align*} \tag{12}
\]

These can be approximated by
\[ \begin{align*}
1 &= C_{pp,11} X_1^0 + C_{pn,10} Y_0^0, \\
0 &= C_{pp,22} X_2^0, \\
0 &= C_{pp,ii} X_i^0 \quad (i = 3, 4, \ldots), \\
1 &= C_{np,01} X_1^0 + C_{nn,00} Y_0^0.
\end{align*} \tag{13}
\]

with the solution
\[ \begin{align*}
X_1^0 &= (C_{nn,00} - C_{pn,10}) \delta^{-1} = a \delta^{-1}, \\
Y_0^0 &= (C_{pp,11} - C_{np,01}) \delta^{-1} = \beta \delta^{-1}, \\
X_2^0 &= C_{pp,22} X_1^0 + C_{pn,20} Y_0, \\
X_i^0 &= 0 \quad (i = 3, 4, \ldots),
\end{align*} \tag{14}
\]

where
\[ \delta = C_{pp,11} C_{nn,00} - C_{pn,10} C_{np,01}. \tag{15} \]

From the Eqs. (14), using (7) and the definitions (4) the usual expression for the field-free viscosity of the mixture is obtained:
\[ \eta_{\text{mix}} = -k T \delta^{-1} (X_p a + X_n \beta). \tag{16} \]

Subtracting now the field-free Eqs. (12) from the general system (11) and neglecting small terms the two sets of equations
\[ \begin{align*}
0 &= C_{pp,11} \Delta X_1 + C_{pp,12} \Delta X_2 + C_{pn,10} \Delta Y_0, \\
0 &= C_{np,01} \Delta X_1 + C_{np,02} \Delta X_2 + C_{nn,00} \Delta Y_0
\end{align*} \tag{17} \]
and
\[ \begin{align*}
0 &= C_{pp,22} \Delta X_2 + \sum \frac{k}{3} F_{k2} X_k, \\
0 &= C_{pp,ii} X_i + F_{i2} X_2 + F_{i2} \Delta X_2
+ \sum \frac{j}{3} F_{jik} X_k \quad (i = 3, 4, \ldots)
\end{align*} \tag{18} \]

are obtained. The set (18) refers only to vectors belonging to \( \mathbb{K}_p \), the subspace of \( \mathbb{H}_p \) orthogonal to \( \mathbb{K} \), and is completely equivalent in \( \mathbb{K}_p \) to the operator equation
\[ C_{pp}^{(0)} \Delta X + F \Delta X = 0 \tag{19} \]
where \( C_{pp}^{(0)} \) is the diagonal part of \( C_{pp} \). The solution of (19) is
\[ \Delta X = -(C_{pp}^{(0)} + F)^{-1} F X^e \tag{20} \]
and in particular
\[ \Delta X_2 = -(C_{pp}^{(0)} + F)^{-1} F X^e_{22} X_2^0. \tag{21} \]

This can be substituted into the set (17), to get
\[ \Delta X_1 + \Delta Y_0 \text{ and hence the change in the viscosity} \]
\[ \Delta \eta = -k T (x_p \Delta X_1 + x_n \Delta Y_0). \tag{22} \]

The field dependence is already completely contained in (21). Comparing this to Eq. (A-25) of I giving the field dependence of the effect for a pure gas, one sees that the forms are identical, except for the substitution of \( \mathcal{C}^{(0)} \) with
\[ C_{pp}^{(0)} = x_p \mathcal{C}_{pp}^{(0)} + x_n \mathcal{C}_{np}^{(0)}. \tag{23} \]

A consequence of this is that the field effect is approximately given by the function \( f_\xi(\xi) \) from Mikhailova and Maskimov’s theory \(^4\), with the parameter \( \xi \) inversely proportional to a collision frequency linear in the concentration, i.e. with a half-field linear in the concentration.
\[ \xi \text{ is given by} \]
\[ \xi = \frac{\omega_{\text{prec}}}{X_p \omega_{pp} + X_n \omega_{pn}}. \tag{24} \]

where \( \omega_{\text{prec}} \) is the precession frequency and \( \omega_{pp} \) and \( \omega_{pn} \) are collision frequencies for p-p and p-n collisions respectively. Hence the half-field is given by
\[ (E/p)_{\frac{1}{2}} = (E/p)_{\frac{1}{2}} x_p = (x_p + x_n \gamma) \tag{25} \]

where \( \gamma = \omega_{pp}/\omega_{pp} \).

It is remarkable that the Levi-McCourt-Tip (LMT) approximation \(^5\) would lead to a half-field of the form
\[ (E/p)_{\frac{1}{2}} = (a x_p + b x_n)^{\frac{1}{2}} c x_p + d x_n \tag{26} \]
non-linear in the concentration: the \((E/p)_{\frac{1}{2}} \) vs. \( x_p \) curve would be concave downwards.

To obtain the saturation value, one has to solve the set (17), using (14) and (21), and then to substitute into (22). The result has a rather complicated form. However, because of time-reversal, the following equalities hold:
\[ C_{pp,12} = \varepsilon_2 C_{pp,21}; C_{pn,10} = \varepsilon_2 C_{np,01}; C_{pn,20} = \varepsilon_2 C_{np,02}. \tag{27} \]

where \( \varepsilon_2 \) is 1 if \( \psi_2 \) is even under time reversal, -1 if it is odd. With the help of these relations the saturation value can be written
\[ (\eta^{-1} \Delta \eta)_{\text{sat}} = -\varepsilon_2 x_p \left( C_{pp,22} + C_{pn,20} \right)^2 \left( x_p + x_n \beta \right)^2 \tag{28} \]
which agrees with Tip’s result \(^6\) when \( \psi_2 \) is taken to be proportional to \([J]^{(2)}\), in which case \( \varepsilon_2 \) is 1.
Formula (28) can be rewritten with the help of the effect for the pure polar gas:

\[
\left( \frac{\Delta \eta}{\eta} \right)_{\text{sat}} = \left( \frac{\Delta \eta}{\eta} \right)_{\text{sat}, x_p = 1} x_p \eta_p n_{\text{mix}} \left( \frac{x_p + x_n}{\eta_p} \right) \frac{r_{\text{pp}, 21} \left( x_p + x_n (\beta/\alpha) \right)}{(x_p + x_n (\beta/\alpha))^{2}}
\]

and taking into account the kinematic factors

\[
\left( \frac{\Delta \eta}{\eta} \right)_{\text{sat}} = \left( \frac{\Delta \eta}{\eta} \right)_{\text{sat}, x_p = 1} x_p \eta_p n_{\text{mix}} \left( \frac{x_p + x_n}{\eta_p} \right) \frac{r_{\text{pp}, 21} \left( x_p + x_n (\beta/\alpha) \right)}{(x_p + x_n (\beta/\alpha))^{2}}
\]

where the parameter \( \varphi \), given by

\[
\varphi = \frac{2 (m_p + m_n)}{m_n} \frac{r_{\text{pp}, 21}}{r_{\text{pp}, 21}}
\]

is (approximately) the ratio between energetically inelastic collision cross section for p-n and p-p collisions [however, the collision brackets appearing in (31) are non-diagonal and do not represent cross sections proper].

II. Experimental

The experimental method has been described in I. The mixtures were prepared in a 40 liter volume and the concentration was controlled by reading the pressure with a mercury manometer first when only one gas was present, then after the mixing had taken place. Any corrections due to real gas effects were smaller than the reading errors. The experimental error in the concentration was less than 2%.

The mixtures flowed into the apparatus through a non-throttled capillary whose diameter and length were 1 mm and 10 cm respectively. These conditions ensured that no fractioning took place. The gases employed are listed in Table 1, together with their purities.

The four polar gases chosen have very different values of the dipole moment; also the molecular shapes are different, two being prolate and two oblate symmetric tops. Besides, the absolute value of the shear viscosity for these polar gases, with the exception of NF₃, is known from direct measurements; the viscosity of NF₃ was estimated from the thermal conductivity, using the Eucken factor².

Since the capillaries forming the bridge have a rectangular cross section whose height is very small compared to the width, if \( z \) is the field direction and \( x \) the flow direction the only non-vanishing component of the velocity gradient is \( \partial v_x / \partial z \). Then following the nomenclature adopted in Ref. the quantity of interest in the measurements is \( \Delta \eta_{\text{sat}}/\eta_0 \).

The results obtained are plotted in Figs. 1 and 2 as a function of the ratio \( E/p \) (field/pressure) for two typical mixtures at different concentrations. For all gases and all concentrations the experimental points can be fitted well by curves corresponding to the function \( f_1(\xi) \) given by the theory of Mikhailova and Maksimov. From this fit the parameters \( \Delta \eta_{\text{sat}}/\eta_0 \) and \( (E/p)^{1/4} \) can be obtained as a function of the concentration \( x_p \) and are plotted in Figs. 3 to 6.

III. Discussion

In Figs. 3 to 6 the experimental results are compared with theory. On the right, the half-value of the field is plotted versus the concentration. A linear relationship between the two quantities is found for

\[
\Delta \eta/\eta \times 10^4
\]

\[\begin{array}{cccc}
\text{Gases} & \text{NF}_3 & \text{CHCl}_3 & \text{CH}_3\text{Cl} & \text{CH}_3\text{CN} & \text{He} & \text{Ar} \\
\end{array}
\]

Table 1. Purity of the gases employed.

all mixtures in agreement with the theory of Ref. 4 and in contrast to Eq. (26) 17a. This linearity shows that one J-dependent term in the expansion of B_p in the Eq. (1) suffices: in particular, there is no appreciable contribution from terms odd in J 18. On the left of each figure the saturation value of the effect, evaluated from Eq. (30) for several values of Q, is plotted versus the concentration. The comparison with the experimental data, also reported, allows the determination of Q.

Table 2 gives for each mixture the values of γ, r and Q; γ is the ratio between the reorientation frequencies for polar-noble gas collisions and polar-polar collisions, r is the corresponding cross section ratio

$$r = \left(\frac{2 m_a}{m_p + m_a}\right)^{\frac{1}{2}} \gamma$$

and Q gives roughly the cross section ratio for inelastic collisions.

17a The field dependence is given by f_q(ξ) in that approximation where one reorientation relaxation time suffices to describe the phenomenon. The present experiments show this to be the case. In the same approximation any theory, including LMT 5, yields the observed linear dependence of (E/p) 1/2 on x_p; but only IT 3, 4 agrees with the experiments as far as the field dependence is concerned. The authors are indebted to Prof. J. J. M. BEENAKKER and Dr. A. TIP for discussion about these points.

Figs. 3—6. On the left: \((\eta_\text{sat}/\eta_0)\) vs. concentration and theoretical curves for three values of \(q\) (see Figs. 3—6).
On the right: \((E/p)_{1/2}\) vs. concentration.
Finally, for CH$_3$Cl the collision frequency ratio $\gamma_{mw}$ was been determined from non-resonant microwave absorption$^{19}$. The comparison is given in Table 3. The agreement is reasonable, but far from perfect: in particular, the ratio $r_{Ar}/r_{He}$ from microwaves is surprisingly low for this gas, especially if the same ratio for CHF$_3$, also from microwaves, is taken into account.

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